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DETERMINATION OF EPICHLOROHYDRIN
IN POTABLE WATER
JUNE 1982

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USAF Occupational and Environmental Health Laboratory
Aerospace Medical Division (AFSC)
Brooks Air Force Base, Texas 78235

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM			
REPORT NUMBER 2. GOVT ACCESSION N		5. RECIPIENT'S CATALOG NUMBER			
USAF OEHL TR 82-11	AD-A12-0875				
4. TITLE (and Sublifie)		5. TYPE OF REPORT & PERIOD COVERED			
Determination of Epichlorohydrin in Potable Water		1 July 1981 - 29 April 1982			
		6. PERFORMING ORG. REPORT NUMBER			
7. AUTHOR(a)		S. CONTRACT OR GRANT NUMBER(s)			
E.H. Sanders, PhD	•	F33615-81-D-4005			
J.H. Nelson, PhD		Order 0003			
9. PERFORMING ORGANIZATION NAME AND ADDRES	is	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS			
UBTL Division University of Utah Research Inst	itute				
l 520 Wakara Way		·			
Salt Lake City, Utah 84108		12. REPORT DATE			
USAF Occupational Environmental	Heal th	June 1982			
Laboratory Brooks AFB, Texas 78235		13. HUMBER OF PAGES			
14. MONITORING AGENCY NAME & ADDRESS(If differ	ent from Controlling Office)	15. SECURITY CLASS. (of this report)			
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		Unclassified			
		154. DECLASSIFICATION/DOWNGRADING SCHEDULE			
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17. DISTRIBUTION STATEMENT (of the abetract enters	od in Block 20, il different fro	om Report)			
18. SUPPLEMENTARY NOTES					
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19. KEY WORDS (Continue on reverse side if necessary	and identify by block number				
epichiorohydrin					
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Preface

This study was performed by UBTL Division, University of Utah Research Institute, Salt Lake City, Utah 84108 for the USAF Occupational and Environmental Health, Aerospace Medical Division, Air Force Systems Command, Brooks AFB, Texas 78235. This study was performed in accordance with contract no. F33615081-D-4005. Dr E.H. Sanders and Dr J.H. Nelson (UBTL) were principal investigators, and L.L. Rodriguez was project monitor for the USAF Occupational Environmental Health Laboratory. Study was initiated on 1 July 1981 and completed 29 April 1982.



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DETERMINATION OF EPICHLOROHYDRIN IN POTABLE WATER

Introduction

A review of current literature indicates that there are no specific methods available for the determination of epichlorohydrin (ECH) in potable water with sufficient sensitivity to achieve a detection limit (LOD) of approximately ten (10) micrograms per liter. The objective of this work was to develop a useful analytical method for the quantitation of ECH in potable water with an LOD of 10 μ g/liter. A suitable method was successfully developed during the project. The work was accomplished in each of three phases. This report briefly summarizes the work of each phase and provides (in the Appendix) a detailed description of the analytical methodology recommended for the determination of ECH in potable water.

Phase 1

The original plan for this phase of the work was to select a suitable solvent for the extraction of ECH from water and to develop appropriate gas chromatographic (GC) procedures for the quantitation of ECH in the extract. Poor, unacceptable recoveries of ECH from potable water were achieved in initial extraction experiments. The required LOD criterion could not be satisfied. Accordingly, UBTL investigated the possibility of determining ECH using purge and trap procedures. Specifically, EPA Method 501.1 (Purge and Trap) [1] was successfully modified to achieve the required analytical performance. A heated purging cycle as described in EPA Method 603 (Section 9) [2] was found to be necessary for the analysis. In addition, experiments were conducted to optimize GC operating conditions. A complete description of the finalized GC purge and trap method for the determination of ECH is provided in the Appendix.

Phase 2

This phase of the work was used to characterize the method with respect to LOD, precision, and linearity. A set of samples was prepared at each of six different ECH concentrations: 1, 5, 10, 20, 50, and 200

 $\mu g/liter$. Each set was comprised of a minimum of seven samples at the ECH concentration of interest. Each sample was analyzed using the developed GC purge and trap method and the instrument response was recorded relative to the corresponding response for bromoform present in each sample as an internal standard at 10 μg per liter. The results are summarized in Table 1. Two data points (one at 50 $\mu g/L$ and one at 200 $\mu g/L$) were omitted as they were determined to be outliers by t-test. Several blank samples were processed during these experiments. No significant instrumental response was observed for any of the blank samples; therefore, data for blank samples are not included in Table 1.

Limit of Detection

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Epichlorohydrin was detected at a concentration of one (1) microgram per liter (1 $\mu g/L$). However, the relative standard deviation at 1 $\mu g/L$ was 24 %. (See Table 1.) This is sufficiently high, in our estimation, to render the method qualitative only at 1 $\mu g/L$. At this concentration, results are not quantitatively reproducible. The results acquired for ECH at a concentration of ten (10) $\mu g/L$ demonstrated a relative standard deviation of 13% for eight samples. Similar relative standard deviations were observed for the other concentrations investigated. Therefore, the method described in the Appendix is considered quantitative in the range of 10 to 200 $\mu g/L$ and qualitative from 1 $\mu g/L$ to 10 $\mu g/L$. The LOD for the quantitative analysis of ECH using this method is established at 10 $\mu g/L$.

Linearity

The response of the instrument is linear in the ECH concentration range of 1-200 µg/L. This is illustrated in Figure 1, a plot of the mean instrument response observed at each concentration (Table 1) versus ECH concentration. Using mean values, the linear regression equation is:

ECH Concentration (μ g/L) = 0.48 + 0.24 * Instrument Response

for the concentration range 1-200 $\mu g/L$. The correlation coefficient is 0.999.

Table 1
Instrumental Response for ECH at Various Concentrations

ECR Concentration (µg/L)	Relative Instrumental Response*	Mean Response	Standard Deviation of Response	Relative Standard Deviation of Response (%)
1.0	0.138 0.130 0.145 0.174 0.227 0.208 0.145 0.233	0.175	0.0420	24.0
5.0	1.07 0.994 1.50 1.09 1.18 1.20 0.949	1.12	0.183	16.3
10.	2.00 2.28 2.43 2.18 2.64 2.55 2.55	2.30	0.301	13.1
20.	5.65 5.61 5.75 5.47 6.70 4.71 6.45	5.76	0.656	11.4
50.	12.7 15.4 13.9 14.5 14.7 15.3	14.1	1.17	8.3
200.	44.8 46.8 54.6 37.4 49.5 54.9 48.6	48.1	6.02	12.5

^{*}Epichlorohydrin response normalized relative to the response for bromoform at 10 $\mu g/L$.

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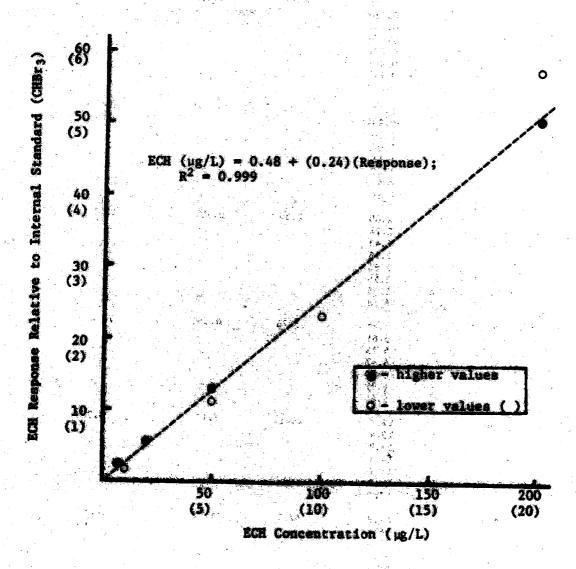


Figure 1. Instrumental Response for Various Concentrations of Epichlorohydrin (ECH) with Bromoform as an Internal Standard.

Bata points at ECH concentrations of 10 and 20 µg/liter are represented on both scales.

Precision

The pooled coefficient of variation (C.V.) for the instrumental response values in the ECH concentration range 10-200 $\mu g/L$ is 11.5%. Thus, the precision of the analytical method is considered adequate for quantitative determinations in this range.

Phase 3

This phase of the work addressed the stability of ECH in potable water in connection with sample storage conditions.

During the preparation of the test samples required for Phase 3, three additional sample sets, each comprised of 13 samples, were prepared. Each of these sample sets contained 13 samples at the same ECH concentration. Sets were prepared at 1, 10, and 200 µg (ECH)/L. For each set, three samples were analyzed after storage (protected from light) at 4°C for two weeks; and four additional samples (only three additional samples at 200 µg/L) were analyzed following storage (protected from light) at 4°C for a period of four weeks. An identical protocol was followed for samples stored at 24°C excepting only three samples (instead of four) were analyzed at each concentration after four-week storage. Upon reaching the specified storage time under the described conditions, the test samples were spiked with bromoform (10 µg/L) (internal standard) and analyzed as were the Phase 2 test samples. The results of these experiments, normalized relative to the bromoform internal standard, are recorded in Table 2.

It is readily apparent that storage conditions profoundly influence instrumental response, i.e., the recovery of ECH. Other variables equal, better ECH recovery was observed for samples stored at 4°C versus those maintained at 24°C. A storage time of two weeks resulted in better ECH recovery than one of four weeks, other parameters invariant. The results presented in Table 2 were used to calculate percent recovery of ECH relative to the corresponding Phase 2 normalized responses (Table 1). The mean value of the instrumental response was used for each set of experimental conditions. The high recovery of 153% observed at 1 μ g/L, 4°C, and two weeks is considered an anomaly.

Table 2 Instrumental Response for ECH at Various Concentrations for Samples Stored at 4° and 24°C

ECH Concentration (µg/L)	Storage Temperature (°C)	Storage Time (Weeks)	Relative Instrumental Response*	Mean Response	Standard Deviation of Response	Relative Standard Deviation of Response (%)	ECH Recovery
1.0	4	2	0.378 0.209 0.216	0.268	0.0956	35.7	153.
	4	. 4	0.022 0.126 0.281 0.172	0.150	0.107	71.3	85.7
	24	2	0.033 0.097 0.062	0.0640	0.0320	50.0	36.€
	24	4	0.000 0.000 0.000	0.	0.	0.	0.
10.	4	2	2.20 2.03 2.14	2.12	0.0862	4.1	92.2
4	4	4	1.74 1.98 1.43 1.49	1.66	0.252	15.2	72.2
	24	2	1.04 1.08 1.26	1.13	0.117	10.4	48.9
	24	4	0.283 0.288 0.145	0.239	0.0812	34.0	10.4
200.	4	2	33.2 37.8 45.5	38.8	6.21	16.0	80.7
	4	4	20.7 28.4 24.1	24.4	3.86	15.8	50.7
	24	2	8.05 3.67 7.90	6.54	2.49	38.1	13.6
	24	4	1.86 1.54 1.16	1.52	0.350	23.0	3.2

^{*}Epichlorohydrin response relative to the response for bromoform at 10 $\mu g/L$. †Percent recovery of epichlorohydrin relative to unstored samples at same concentration.

A plot of the percent recovery versus storage time is presented in Figure 2. The 153% recovery data point at $\mu g/L$ has been omitted. The plot demonstrates conclusively that a clean field sample taken for the analysis of epichlorohydrin by this method must be maintained at 4°C and analyzed within 7 days of sampling. Only by strict adherence to these conditions can the analytical results be considered quantitatively representative (within 10 percent) of the concentration at the time of sampling. The plot also indicates a more rapid decomposition of the sample with increasing concentration. This phenomenon could possibly be attributed to autocatalysis of the decomposition process and will render analytical results for samples with ECH concentrations greater than 100 micrograms per liter suspect unless analysis is conducted immediately following sampling. In addition, these results and conclusions were obtained with test samples prepared from distilled deionized water, free of organic contaminants. Actual field samples would not be composed of the same sample matrix and obviously could contain material which would enhance the rate of decomposition even in samples which are refrigerated at 4°C. Analytical results of samples which have not been properly refrigerated should not be considered quantitatively valid.

Summary

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An analytical method for the quantitative determination of epichlorohydrin ECH in the concentration range 10-100 $\mu g/L$ has been developed. The method consists of gas chromatographic/purge and trap procedures. The LOD is 10 $\mu g/L$; the pooled coefficient of variation is approximately 10% (10-100 $\mu g/L$). ECH recovery is highly dependent on storage conditions (temperature and time) and on ECH concentration. Quantitative results are suspect if sample storage temperature and time exceed 4°C and seven days, respectively, and if the ECH concentration exceeds 100 $\mu g/L$. Any compound which co-elutes with ECH under the GC/purge and trap conditions specified is considered an interference. Neither a study of possible interferences nor sample matrix effects has been investigated.

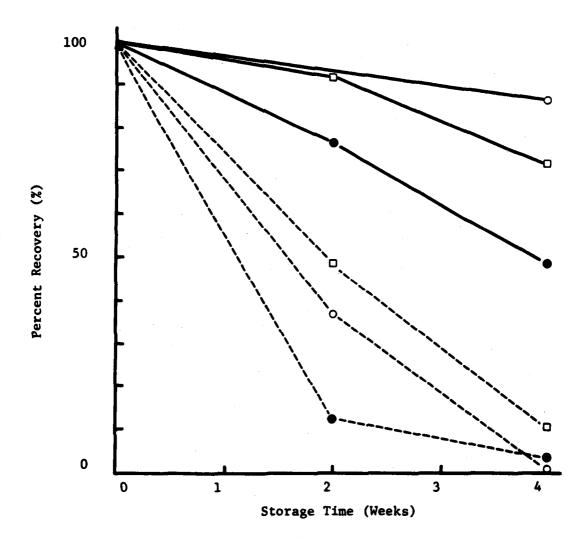


Figure 2. Results of Storage Study to Determine the Percent Recovery for Epichlorohydrin in Distilled Deionized Water at Concentrations of 1 μ g/L (\circ), 10 μ g/L (\circ), and 200 μ g/L (\circ) at 4°C (\longrightarrow) and 24°C (\longrightarrow).

The developed analytical method is described in detail in the Appendix.

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APPENDIX

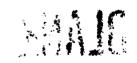
Methodology for Analysis of of Epichlorohydrin in Potable Water

UBTL Division
University of Utah Research Institute
Salt Lake City, Utah 84108

FOREWORD

This method has been prepared by the staff of the Chemistry Department of the UBTL Divison of UURI at the request of the USAF Occupational and Environmental Health Laboratory, Air Force Systems Command. The method is a modification of U.S. Environmental Protection Agency (EPA) Method 501.1; Figures 2-4 are reproductions taken directly from this published EPA methodology. Comments and suggestions offered by the U.S. Environmental Protection Agency are gratefully acknowledged.

The procedure represents the current state of the art, but as time progresses improvements are anticipated. Users are encouraged to identify problems and assist in updating the method by contacting the UBTL Divison of the University of Utah Research Institute, Salt Lake City, Utah 84108.



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METHODOLOGY FOR ANALYSIS OF EPICHLOROHYDRIN

1. Scope and Application

- 1.1 This method is applicable to the determination of epichlorohydrin in potable water and in municipal and industrial discharges. As such, it presupposes a high expectation of finding the specific compound of interest (epichlorohydrin). If the user is attempting to screen samples for epichlorohydrin, he must develop independent protocols for the verification of identity as suggested in Section 7.2.
- 1.2 The sensitivity of this method is generally dependent upon the level of interferences rather than instrumental limitations.

 The limit of detection represents a sensitivity that can be achieved in water under optimum operating conditions.
- 1.3 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. Summary of Method

2.1 An inert gas is bubbled through a 5-ml water sample contained in a specially-designed heated purging chamber. Epichlorohydrin and other volatile organic compounds are transferred from the liquid phase to the gaseous phase. The vapor is passed through a short sorbent tube where the compounds are trapped. After the extraction is completed, the trap is heated and backflushed with gas to desorb the compounds into a gas chromatographic (GC) system. A temperature program is used in the GC system to separate the compounds before detection with a Hall electrochemical conductivity detector.

3. Interferences

3.1 Impurities in the purge gas and organic compounds out-gasing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from interferences under the conditions

- of the analysis by running method blanks. Method blanks are run by charging the purging device with organic-free water and analyzing it in a normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.
- 3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride) through the septum seal into the sample during shipment and storage. A sample blank prepared from organic-free water and carried through the sampling and handling protocol can serve as a check on such contamination.
- 3.3 Cross contamination can occur whenever high-level and low-level samples are sequentially analyzed. To reduce the likelihood of this, the purging device and sample syringe should be rinsed out twice between samples with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free water to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds, or high organohalide levels; it may be necessary to wash out the purging device with a soap solution, rinse with distilled water, and then dry in a 105°C oven between analyses.
- 3.4 Interferences are sometimes reduced or eliminated by first purging the water sample for 5 minutes at room temperature in 9.4. Then the purge device is rapidly heated to 85°C and purged as in 9.4. With such a modification, a trace of the epichlorohydrin in the sample will be lost. Therefore, if this modification is implemented, calibration must be established for epichlorohydrin under the conditions of this modified procedure.

4. Apparatus and Materials

- 4.1 Sampling equipment, for discrete sampling.
 - 4.1.1 Vial, with cap 40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry at 105°C before use.

- 4.1.2 Septum Teflon faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105°C for one hour before use.
- 4.2 Purge and trap device The purge and trap equipment consists of three separate pieces of apparatus: the purging device, trap, and desorber. The purging device should be equipped for heating in the same manner as the trap (electrically) or with a circulating water jacket. If electrical heating is used, the electrical parts must be protected so that water will not drip on the conductors causing dangerous electrical shock. All temperature parameters must be carefully controlled. Several complete devices are available commercially although most are not equipped to heat the purging chamber as required. The device must meet the following specifications: the unit must be completely compatible with the gas chromatographic system; the purging chamber must be designed for a 5 ml volume and be modeled after Figure 1; the dimensions for the sorbent portion of the trap must meet or exceed those in Figure 2. Figures 3 and 4 illustrate the complete system in the purge and the desorb mode, respectively.
- 4.3 Gas chromatograph Analytical system complete with programmable gas chromatograph suitable for on-column injection and all required accessories including column supplies, recorder, gases, and a halide-specific detector such as the Hall detector outlined in Figure 5. A data system for measuring peak areas is recommended.
- 4.4 Syringes 5-ml glass hypodermic with Leurlok tip (2 each).
- 4.5 Micro syringes 10, 25, 100 μ1.
- 4.6 Two-way syringe valve with Leur ends (3 each).
- 4.7 Bottle -1 15-ml screw-cap, with Teflon cap liner.

5. Reagents

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- 5.1 Preservatives
 - 5.1.1 Sodium hydroxide (ACS) 10 N in distilled water.

- 5.1.2 Sulfuric acid (ACS). Mix equal volumes of concentrated ${\rm H_2SO_{\Delta}}$ with distilled water.
- 5.1.3 Sodium thiosulfate (ACS) granular.
- 5.2 Trap absorbent

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- 5.3 Activated carbon Filtrasorb-200 (Calgon Corporation) or equivalent.
- 5.4 Organic-free water
 - 5.4.1 Organic-free water is defined as water free of interference when employed in the purge and trap procedure described herein. It is generated by passing tap water through a carbon filter bed containing about 1 lb. of activated carbon.
 - 5.4.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water.
 - 5.4.3 Organic-free water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow mouth screw-cap bottle and seal with a Teflon lined septum and cap.
 - 5.4.4 Organic-free water may also be prepared by processing deionized water in a Sybron-Barnstead ORGANICpure unit which removes organic impurities by an ultraviolet light oxidation process.
- 5.5 Stock standards Prepare stock standard solutions daily in water using assayed standards. Because of toxicity, primary dilutions of epichlorohydrin should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be used when the analyst handles high concentrations of this material.
 - 5.5.1 Place about 9.8 ml of methanol into a 10-ml ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

- 5.5.2 Using a 100-µl syringe, immediately add 2 drops of assayed epichlorohydrin reference material to the flask, then reweigh. Be sure that the 2 drops fall directly into the methanol without contacting the neck of the flask.
- 5.5.3 Dilute to volume, stopper, then mix by inverting the flask several times. Transfer the standard solution to a 15-ml screw-cap bottle with a Tefon cap liner.
- 5.5.4 Calculate the concentration in micrograms per microliter from the net gain in weight.

6. Calibration

- 6.1 Using stock standards, prepare secondary dilution standards in water. The standards should be prepared at concentrations such that the aqueous standards prepared in 6.2 will completely bracket the working range of the chromatographic system.
- 6.2 Using secondary dilution standards, prepare calibration standards by carefully adding μl of stock standard to 100, 500, or 1000 ml of organic-free water.
- 6.3 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table 1. By injecting secondary dilution standards, establish the calibration curve and linear range of the analytical system for epichlorohydrin.
- 6.4 Assemble the necessary purge and trap device. The trap must meet the minimum specifications as shown in Figure 2 to achieve satisfactory results. Condition the trap overnight at 180°C by backflushing with an inert gas flow of at least 20 ml/minute. Prior to use, daily condition traps 10 minutes while backflushing at 180°C. Analyse aqueous calibration standards (6.2) according to the purge and trap procedure in Section 9. Compare the responses to those obtained by injection of standards (6.3), to determine purging efficiency and also to calculate analytical precision. The purging efficiencies and analytical precision of the analysis of aqueous standards should be 85 ± 5%.

6.5 By analyzing calibration standards, establish the sensitivity limit and linear range of the entire analytical system for epichlorohydrin.

7. Quality Control

- 7.1 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water method blank that the entire analytical system is interference-free.
- 7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis.

Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

7.3 The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and blank with surrogate compounds.

8. Sample Collection, Preservation, and Handling

- 8.1 Collect about 500 ml sample in a clean container. Adjust the pH of the sample to 6.5 to 7.5 by adding 1:1 diluted H₂SO₄ or NaOH while stirring vigorously. If the sample contains residual chlorine, add 35 mg of sodium thiosulfate per part per million of free chlorine per liter of sample. Fill a 40-ml sample bottle and seal the bottle so that no air bubbles are entrapped in it. Maintain the hermetic seal on the sample bottle until time of analysis.
- 8.2 The samples <u>must</u> be iced or refrigerated at 4°C from the time of collection until analysis.
- 8.3 All samples must be analyzed within 7 days of collection.

9. Sample Extraction and Gas Chromatography

- 9.1 Adjust the helium purge gas flow rate to 20 ± 1 ml/minute and the temperature of the purge device to 85°C. Attach the trap inlet to the purging device, and set the device to purge. Open the syringe valve located on the purging device sample introduction needle.
- 9.2 Remove the plunger from a 5-ml syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the water into the syringe barrel until it overflows. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 ml.
- 9.3 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.
- 9.4 Close both valves and purge the sample for 30.0 ± 0.1 minutes. Monitor and control the temperature of the purge device to obtain $85 \pm 1^{\circ}$ C.
- 9.5 After the 30-minute purge time, attach the trap to the chromatograph, and adjust the device to the desorb mode. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with helium at 45 ml/minute for 5 minutes. The backflushing time and gas flow rate must be carefully reproduced from sample to sample. During backflushing, the chromatographic column is held at 100°C. Record GC retention time from the beginning of desorption.
- 9.6 While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5-ml portions of organic-free water.
- 9.7 After desorbing the sample for 5 minutes, recondition the trap by returning the purge and trap device to the purge mode and begin the GC program. Wait 15 seconds, then close the syringe

valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately 7 minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

9.8 Table 1 summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. Calibrate the system daily by analysis of a minimum of three concentration levels of calibration standards.

10. Calculations

- 10.1 Determine the concentration of epichlorohydrin directly from calibration plots of concentration ($\mu g/1$) versus peak height or area units.
- 10.2 Report results in micrograms per liter. When duplicate and spiked samples are analyzed, all data obtained should be reported.

11. Accuracy and Precision

Insufficient data have been accumulated for the complete statistical determination of accuracy and precision of this analytical methodology.

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TABLE 1
Gas Chromatography by Heated Purge and Trap

		Limit of	Limit of Quantitation	
		Detection		
Compound	Retention Time (min.)	<u>μg/1</u>	μ g /1	
Epichlorohydrin	9.2	1.0	10	

Column and Analytical Conditions: Carbopack C (60/80 mesh) coated with 0.2% Carbowax 1500 and packed into a 6 foot long x 2-mm ID Pyrex glass column with a helium carrier gas at a flow rate of 40 ml/minute. Temperature program - Initial 70°C, hold for 3 minutes, then program at 5°C/minute to 160°C, and hold for 4 minutes or until all compounds have eluted.

Detection limit is estimated based upon the use of an electrolytic conductivity detector in the halogen specific mode and a sample size of 5 ml.

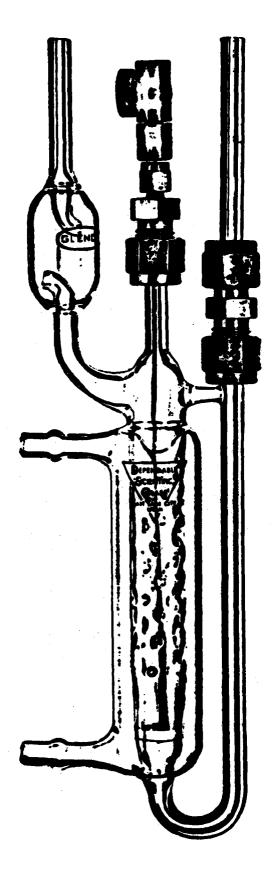
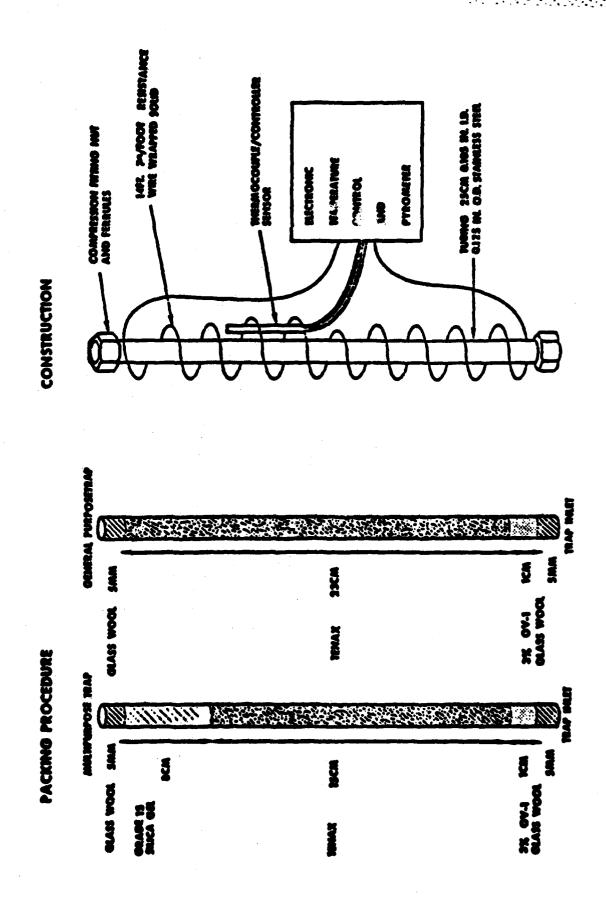
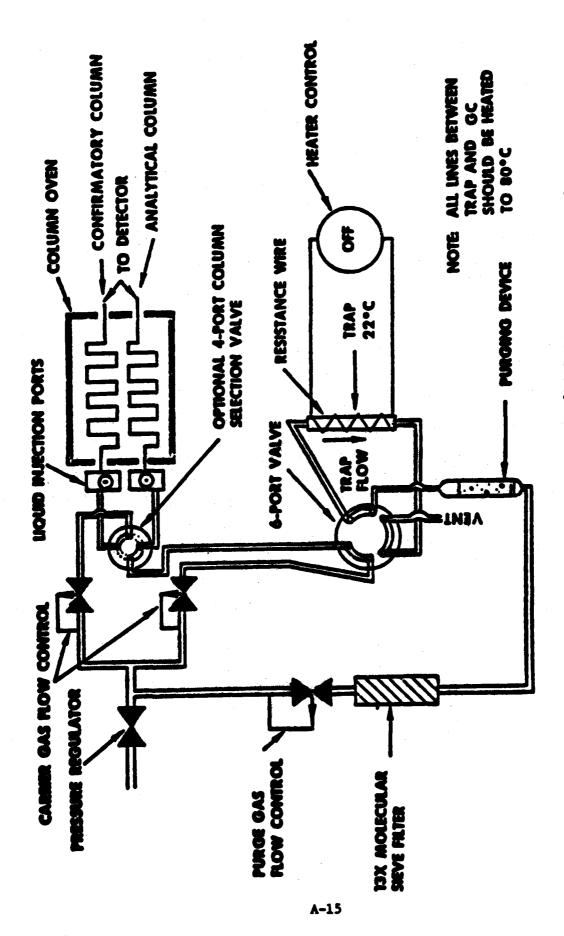


Figure 1. Heated Purging Device





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(PURGE-SORB MODE) FIGURE 3 PURGE-TRAP SYSTEM

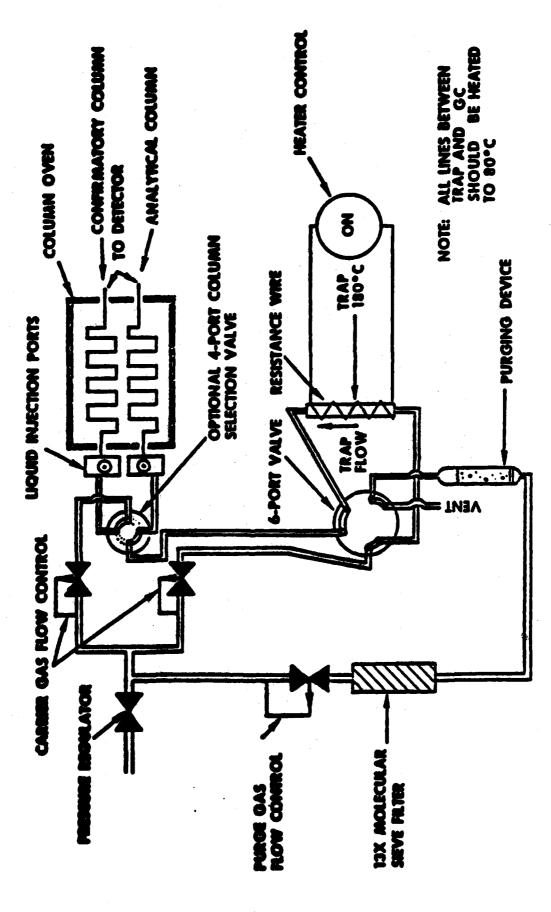
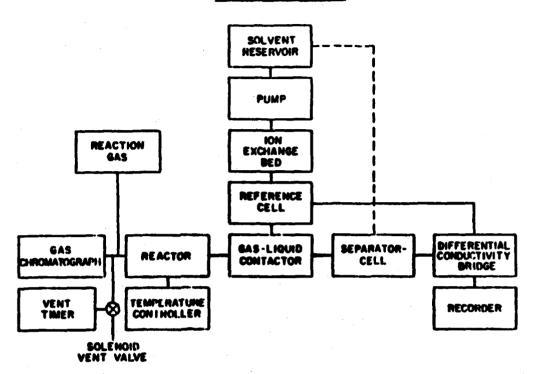


FIGURE 4 PURGE-TRAP SYSTEM (DESORB MODE)

HECD SCHEMATIC



HALL DETECTOR (HECD)

REDUCTION MODE - HALOGEN ANALYSIS $RX + H_2 \xrightarrow{850^{\circ}C} HX$ H_2O

- ORGANIC COMPOUNDS ARE MIXED WITH HYDROGEN, PASSED THROUGH A MICROREACTOR AND GASEOUS.HX PRODUCTS FORMED
- REACTION PRODUCTS ARE MIXED WITH SOLVENT AND MEASURED IN A CONDUCTIVITY CELL
- GOOD SENSITIVITY; EXCELLENT SELECTIVITY.



Figure 5. HALL DETECTOR